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Applicant: Okamoto Chemical Industry Corporation

Inventors: Shoji SAKAMOTO et al.

Representatives: Patent Attorney, Hisao OKUYAMA et al.

[Title of the Invention] ALUMINUM SUPPORT FOR LITHOGRAPHIC PRINTING PLATE AND METHOD FOR PRODUCING THE SAME

[Abstract]

[Object] An object of the present invention is to provide an aluminum support for a lithographic printing plate produced by electrolytically polishing an aluminum plate (including an aluminum alloy plate) and etching the aluminum plate with an alkali, which has a surface having a specified average roughness, a specified diameter of pits and a specified pit dispersion state and is also excellent in reproducibility, and a method for producing the same.

[Constitution] The aluminum support for a lithographic printing plate of the present invention is a lithographic printing plate, which is produced by electrolytically polishing an aluminum plate and etching the aluminum plate with an alkali to form pits on the surface, wherein (a) a centerline average roughness Ra of the surface is from 0.05

to 0.25 µm, (b) at least 80% of the surface area is provided with pits having a diameter of 0.01 to 1.5 µm, and (c) surface reflectivity is at least 50%. A method for producing the same comprises performing electrolytic polishing in an electrolytic solution containing hydrochloric acid, boric acid and aluminum ions.

Photograph substituted for drawing

[Claims]

[Claim 1] An aluminum support for a lithographic printing plate, which is produced by electrolytically polishing an aluminum plate and etching the aluminum plate with an alkali to form pits on the surface, wherein

(a) a centerline average roughness Ra of the surface is from 0.05 to 0.25 μm,

(b) at least 80% of the surface area is provided with pits having a diameter of 0.01 to 1.5 μm, and

(c) surface reflectivity is at least 50%.

[Claim 2] A method for producing the aluminum support for a lithographic printing plate of claim 1, which comprises performing electrolytic polishing in an electrolytic solution containing hydrochloric acid, boric acid and aluminum ions using a three-phase current.

[Detailed Description of the Invention]

[0001]

[Filed of Industrial Application] The present invention relates to an aluminum support for a lithographic printing plate and a method for producing the same. More particularly, it relates to an aluminum support for a lithographic printing plate produced by electrolytically polishing an aluminum plate (including an aluminum alloy plate) and etching the aluminum plate with an alkali, which has a surface having a specified average roughness, a specified diameter of pits and

a specified pit dispersion state and is also excellent in reproducibility, and a method for producing the same.

[0002]

[Prior Art] Lithographic printing is a printing system that utilizes properties comprising the region which receives water to repel an oil base ink (non-image area) and the region which repels water to receive an oil base ink (image area). Therefore, it is required that a support used in a lithographic printing plate is excellent in water retention, reproducibility of images, and adhesion. Thus, the surface of an aluminum plate used as the support for lithographic printing is grained by mechanical, chemical and/or electrochemical methods.

[0003] Water retention and plate wear have recently been improved by forming pits (pores) on the aluminum surface by electrochemical polishing (electrolytic polishing) and specifying the size, depth and dispersion state. Known examples include, for example, Japanese Unexamined Patent Publication (Kokai) No. 53-133903, Japanese Unexamined Patent Publication (Kokai) No. 55-128494 and Japanese Unexamined Patent Publication (Kokai) No. 59-182967. In these methods described in the above publications, the average roughness Ra is at least 0.6 μm, and at least 50% of the surface area is provided with pits having a diameter of at least 3 μm.

[0004]

[Problems to be Solved by the Invention] The above-mentioned grained surface is excellent in water retention and plate wear, however, the following improvements are required.

(1) Because of large surface roughness of the grained surface, sharpness of images formed thereon and reproducibility are poor.

(2) The photosensitive film formed on the grained surface is not uniform, and thus uniform ink buildup is not obtained and the density of the resulting print varies.

(3) Since the grained surface is rough and uneven, air or water penetrates into the space between the ink and the image, uniform ink buildup is not obtained.

(4) Since the grained surface is uneven, when the surface is wiped off with a sponge or a cloth, a sponge residue or a rubber may be deposited.

(5) When unnecessary positions other than images are erased with an erasing solution, the resist remained on the bottom of the grain rises to the surface due to the erasing solution thereby to cause contamination.

[0005] The present inventors have found that, by controlling the average roughness of the grain to not more than 0.25 μm and specifying the diameter of pits within a specific range and its distribution, it is made possible to make an aluminum support for a lithographic printing plate which is excellent in sharpness of images and reproducibility and can attain

uniform ink buildup due to squeezing of water, and also causes neither sponge residue nor contamination of erasure trace because of smooth surface.

[0006]

[Means for Solving the Problems] The present invention provides an aluminum support for a lithographic printing plate, which is produced by electrolytically polishing an aluminum plate and etching the aluminum plate with an alkali to form pits on the surface, wherein (a) a centerline average roughness Ra of the surface is from 0.05 to 0.25 μm, (b) at least 80% of the surface area is provided with pits having a diameter of 0.01 to 1.5 μm, and (c) surface reflectivity is at least 50%, and the aluminum support for a lithographic printing plate of claim 1, wherein electrolytic polishing is performed in an electrolytic solution containing hydrochloric acid, boric acid and aluminum ions using a three-phase current, and a method for producing the aluminum support for a lithographic printing plate of claim 1, which comprises performing electrolytic polishing in an electrolytic solution containing hydrochloric acid, boric acid and aluminum ions using a three-phase current.

[0007] The present invention will now be described. The aluminum plate used in the present invention includes a plate-shaped material made of an aluminum alloy containing pure aluminum and a trace amount of heteroatoms.

[0008] Examples of the heteroatom include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel and titanium atoms. These heteroatoms are used in the content of not more than 10% by weight.

[0009] In the method of the present invention, first, the surface of an aluminum plate is preferably pretreated so as to expose clean aluminum surface by removing a rolling oil on the aluminum surface. For example, the pretreatment is performed by cleaning with a solvent or a surfactant, or etching with an alkali agent. After the completion of the pretreatment, the aluminum plate is sufficiently washed with water and then subjected to an electrolytic polishing treatment.

[0010] An electrolytic solution used in the electrolytic polishing treatment may be a mixed solution of one or more kinds of nitric acid, hydrochloric acid and a salt thereof, containing dissolved aluminum ions. If necessary, the electrolytic solution may contain corrosion accelerators, corrosion inhibitors and stabilizers, for example, nitric acid, phosphoric acid, chromic acid, boric acid, nitrate, chloride, ammonium salt, and amines.

[0011] It is preferred that the electrolytic solution contains 0.1 to 15% by weight of the above acids and the content of dissolved aluminum ions in the electrolytic solution is maintained within a range from 0 to 50 g/l.

[0012] In the present invention, an electrolytic solution having most preferable composition contains 35 to 80 g/l of hydrochloric acid (hydrochloric acid containing 35% by weight of hydrogen chloride is used), 4.0 to 25 g/l of boric acid and 20 to 40 g/l or aluminum ions.

[0013] When the content of hydrochloric acid is 80 g/l or more, deep and large pits having a diameter of 5 μm or more may be formed un-uniformly. On the other hand, when the content of hydrochloric acid is 35 g/l or less, it becomes difficult to flow electric current and an electrolytic voltage must be increased, resulting in high power consumption and high cost.

[0014] When the content of boric acid is 25 g/l or more, pits are scarcely formed because a polishing ability is adversely affected. On the other hand, when the content of boric acid is 4.0 g/l or less, it becomes impossible to form fine pits having a diameter of 0.01 to 1.5 μm, and thus the addition effect is not exerted.

[0015] Electric current used in the electrolytic polishing treatment is a single-phase current or a three-phase current, and preferably an electric current of an alternating wave such as sine wave having a frequency within a range from 10 to 200 Hz, partially cut wave obtained by a thyristor, or symmetrical or asymmetrical wave having a ratio (+)/(-) of less than 30%.

[0016] The present inventors have intensively studied about the shape of graining. As a result, it has been found that preferable electric power applied to the aluminum plate is as follows: the voltage is from about 5 to 35 V, the electric current is from 10 to 40 A/dm^2, and the quantity of electricity is from about 50 to 1000 coulomb. The temperature of the electrolytic solution is from about 20 to 50°C and the distance between electrodes and aluminum is from 1 to 10 cm.

[0017] The electrolytically polished aluminum plate is sufficiently washed with water and then etched with an alkali so as to open the shape of pits formed by electrolytic polishing and to whiten the surface thereby to control surface reflectivity to 50% or more. When alkali etching is omitted, the group of pits having uniform diameter and distribution may not be formed and the polishing residue causes blackening of the surface. Therefore, when the resulting aluminum plate is used as a photosensitive printing plate, the sensitivity decreases and contamination arises.

[0018] Examples of the alkali agent used in alkali etching include sodium hydroxide, potassium hydroxide, sodium tertiary phosphate, potassium tertiary phosphate, sodium aluminate, sodium carbonate, sodium metasilicate, sodium orthosilicate, and sodium gluconate. A solution of these alkali agents alone or a mixture thereof can be used.

[0019] The alkali content of the alkali etching solution is preferably from 1 to 60% by weight, and etching is performed at a liquid temperature of 30 to 100°C and an etching rate of 0.5 to 13 g/m^2 for 2 to 60 seconds. Examples of the etching method include a method of dipping an aluminum plate in an etching bath, a method of coating with an alkali solution using a spray or a nozzle, and a method of etching by flowing a liquid through a slit-shaped port.

[0020] As described above, according to the present invention, there can be produced an aluminum plate wherein an average roughness of the surface is from 0.05 to 0.25 μm, at least 80%, preferably at least 85%, of the surface area of the aluminum plate is provided with pits having a diameter of 0.01 to 1.5 μm, and surface reflectivity is at least 50% by selecting the composition of the electrolytic solution, electrolytic plating conditions and alkali etching conditions. On the other hand, the remained portion of the surface area of the aluminum plate may be provided with pits having a diameter of 0.01 μm or less and/or 1.5 μm or more.

[0021] After the completion of the alkali etching of the aluminum plate, smut is preferably removed with nitric acid, phosphoric acid, sulfuric acid, chromic acid, or an acid mixture containing two or more kinds of these acids, or smut is removed by washing with water or washing with water under high pressure (3 kg/cm^2 or more).

[0022] The aluminum plate is optionally subjected to an anodizing treatment and the subsequent chemical treatment for the purpose of preventing scratch of the surface or fixing a photosensitive layer more firmly.

[0023] The anodizing treatment can be performed in accordance with a known method. For example, an anodic oxide film is formed on the surface of the aluminum plate by anodizing in an aqueous solution of nitric acid, phosphoric acid, chromic acid, oxalic acid or a mixture thereof as an electrolytic solution under direct or alternating current flow.

[0024] If necessary, the aluminum plate anodized described above can be subjected to a sealing treatment such as boehmite treatment with hot water, or a silicate treatment with sodium silicate or potassium silicate, or provided with an under coat made of hydrophilic cellulose or polyvinylphosphonic acid.

[0025] A lithographic printing plate or a photosensitive lithographic printing plate (PS plate) can be made by providing the resulting aluminum support for a lithographic printing plate of the present invention with a conventionally known photosensitive layer. For example, there can be used an aluminum deep-etch plate made of polyvinyl alcohol and dichromates or a water-soluble diazo resin, an aluminum albmen plate, and an aluminum wipe-on plate made of a water-soluble diazo resin and a lacquer.

[0026] As the photosensitive layer for photosensitive lithographic printing, for example, there can be used a photosensitive layer containing a solvent-soluble diazo resin and a water-insoluble and lipophilic polymeric compound having hydroxyl groups, a photosensitive layer made of a mixture of an O-naphthoquinoneazide sulfonate ester and a novolak type phenol or a novolak type cresol resin, a photosensitive layer containing an alkali-soluble polymeric compound, an addition-polymerizable unsaturated compound and a photopolymerization initiator, and a photosensitive layer made of an azide photosensitive material and a novolak type phenol resin.

[0027] It can also be used as a support of a lithographic printing plate for electrophotographic system wherein a zinc oxide-based material and an organic photoconductor can be used as a photosensitive material.

[0028]

[Operation] The printing plate made by forming the above-mentioned photosensitive layer on the surface of the aluminum support for a lithographic printing plate obtained by the method of the present invention is excellent in reproducibility of images and can attain ink buildup with high volume due to squeezing of water, and thus the resulting printing plate causes neither sponge residue nor contamination of erasure trace. The resulting printing plate

is also suited for printing with high accuracy of 500 lines/inch or more. There is also obtained a support capable of improving storage stability of the photosensitive layer.

[0029] The present invention will now be described in detail by way of examples, but is not limited to these examples unless they depart from the spirit or scope of the present invention.

[0030] Examples 1 to 3 and Comparative Example 1

A 0.24 mm thick aluminum plate (material: 1050) was immersed in an aqueous 5% sodium hydroxide solution at 50°C for 10 seconds, degreased and then fully washed with water. The aluminum plate was electrolytically polished with an electrolytic solution shown in Table 1 under the respective conditions using a three-phase current.

[0031] The aluminum plate was washed with water, etched by flowing a 25% caustic soda solution at 70°C, washed with water under high pressure and then subjected to an anodizing treatment in an aqueous 10% sulfuric acid solution at 30°C to form an oxide film (2.0 g/m^2).

[0032] Average roughness and reflectivity of the surface of the resulting aluminum plate are shown in Table 1. The average roughness was measured by using a roughness meter, Model SE-40D, manufactured by Kosaka Laboratory Ltd., while the reflectivity was measured by a meter, Model CM-53P, manufactured by Murakami Color Research Laboratory.

[0033] Electron microscope photographs of the surface of the resulting aluminum plate are shown in Fig. 1 (Example 1), Fig. 2 (Example 3) and Fig. 3 (Comparative Example 1).

[Table 1]

	Composition of electrolytic solution			Liquid temperature (°C)	Current density (A/dm^2)	Electrolysis time (sec)	Average roughness (µm)	Reflectivity (%)
	Hydrochloric acid (g/l)	Aluminum ions (g/l)	Boric acid (g/l)					
Example 1	35	20	10	45	15	6	0.15	55.0
Example 2	35	20	10	45	25	6	0.20	57.5
Example 3	35	20	10	45	30	6	0.25	58.7
Comparative Example 4	35	0	0	45	30	25	0.60	45.6

[0034] As is apparent from the electron microscope photographs shown in Fig. 1 and Fig. 2, at least 80% of the entire surface area of the aluminum plate obtained in the example of the present invention is provided with pits having a diameter of not more than 1.5 μm, and therefore the aluminum plate is excellent in surface uniformity. As is apparent from Fig. 3 (Comparative Example 1), the surface of the aluminum plate is studded with pits having a diameter of at least 5 μm and the condition of the grained surface varies.

[0035] A positive photosensitive lithographic printing plate comprising a photosensitive layer having a dry weight of 2.0 g/m^2 was made by applying the following sensitizing solution on each of the aluminum plates obtained in Examples 1 to 3 and Comparative Example 1.

[0036]

Ester compound of naphthoquinone-(1,2)-diazide-5-sulfonic acid chloride and acetone-pyrogallol resin	2.6 g
Novolak resin (FPS-2803, manufactured by Gunei Chemical Industry Co., Ltd.)	6.0 g
Novolak resin (FPS-2807, manufactured by Gunei Chemical Industry Co., Ltd.)	2.0 g
2-(p-methoxyphenyl)-4,6-bis(trichloromethyl)-S-triazine	0.06 g
Phthalic acid	0.1 g
Oil Blue 613 (manufactured by Orient Chemical Industries, LTD.)	0.15 g

Ethylene glycol monomethyl ether	50 g
Propylene glycol monomethyl ether	50 g

[0037] The photosensitive lithographic printing plate thus obtained was exposed to light from a distance of 1 m under a positive film for 30 seconds, using a 3 KW high pressure mercury vapor lamp. Then, the photosensitive lithographic printing plate was immersed in a developer solution having the following composition at 25°C for 20 seconds to form images.

JIS No. 3 sodium silicate	25 g
Potassium hydroxide	15 g
Cationic surfactant	1 g
Water	1 Kg

[0038] The printing plate was washed with water and then desensitized with a gum arabic solution. The respective printing plates were subjected to the following tests.

(1) Sharpness of images

Halftone dot on the respective printing plates and sharpness of fringe of images are observed. Electron microscope photographs of the halftone dot obtained in Example 1 and Comparative Example 1 are respectively shown in Fig. 4 and Fig. 5.

(2) Ink buildup

Ink buildup on prints obtained by using the respective printing plates and its volume are compared.

(3) Sponge residue

After mounting each of the respective printing plates to a proof press, the surface of the plate is wiped off by a sponge impregnated with water. It is examined weather or not sponge residue is deposited.

(4) Water retention

Water retention and resistance to contamination of the respective printing plates are compared.

(5) Contamination of erasure trace

The unnecessary positions of the respective printing plates are erased with an erasing solution. It is examined whether or not contamination of erasure trace and its profile constitute contamination. The results are shown in Table 2.

[Table 2]

	Sharpness of images	Ink buildup	Sponge residue	Water retention	Erasure trace
Example 1	A	A	A	A	A
Example 2	A	A	A	A	A
Example 3	A	A	A	A	A
Comparative Example 1	C	C	C	A	B

A: Good

B: Slightly poor

C: Poor

[0039] As is apparent from the results shown in Table 2, the printing plates obtained in Examples 1 to 3 are excellent in sharpness of images and degree of ink buildup, and are also

less likely to cause deposition of sponge residue and contamination of erasure trace, and are identical in water retention. These printing plates are excellent printing plates because water can be squeezed. As is apparent from a comparison between Fig. 4 and Fig. 5, the printing plate is excellent in reproducibility because profile of halftone dot in Fig. 4 is not broken.

[0040] Examples 4 to 6 and Comparative Example 2

Each of the aluminum plates obtained in Examples 1 to 3 and Comparative Example 1 was treated in a 5% JIS No. 3 sodium silicate solution at 70°C for 10 seconds and washed with water, and then a solution having the following composition was applied thereon to make a negative photosensitive lithographic printing plate comprising a photosensitive layer having a dry weight of 1.8 g/m^2.

[0041]

Copolymer of 2-hydroxy-3-phenoxypropyl alcohol/methyl methacrylate/acrylonitrile/mono(2-methacryloxyethyl)hexahydrophthalate in a weight ratio of 40/30/10/20	3.0 g
2-methoxy-4-hydroxy-5-benzoylbenzenesulfonate of condensate of 4-diazodiphenylamine and formaldehyde	0.3 g
Victoria Pure Blue BOH (manufactured by HODOGAYA CHEMICAL Co., Ltd.)	0.1 g
Malic acid	0.03 g
Ethylene glycol monomethyl ether	90 g
N-N′-dimethylformamide	10 g

[0042] The negative photosensitive lithographic printing plate thus obtained was exposed to light from a distance of 1 m under a positive film for 30 seconds, using a 3 KW high pressure mercury vapor lamp. Then, the negative photosensitive lithographic printing plate was immersed in a developer solution having the following composition at 25°C for 20 seconds to form images.

Aqueous 20% potassium silicate solution	50 g
Phenyl glycol PGH (manufactured by Nippon Nyukazai Co., Ltd.)	40 g
Potassium isopropylnaphthalene disulfonate	5 g
Potassium sulfite	2 g
Water	903 g

[0043] After washing with water and desensitizing with a gum arabic solution, the respective printing plates were subjected to the following tests.

(1) Sharpness of images

Halftone dot on the respective printing plates and sharpness of fringe of images are observed.

(2) Ink buildup (number of inked prints)

After mounting each printing plate to a printing press, wood free papers were printed using a commercially available ink. The number of prints requited to obtain a print having sufficient ink density was examined. The smaller the numerical value, the better.

(3) Storage stability

The respective photosensitive printing plates before subjecting to the development are allowed to stand in a high moisture atmosphere at a temperature of 30°C and a humidity of 85%, and then exposed, developed and desensitized in the same manner as described above. After mounting to a printing press, it is examined whether or not background contamination of the non-image area occurs.

[0044] The above results are shown in Table 3.

[Table 3]

	Sharpness of images	Ink buildup (number of inked prints)	Water retention
Example 4	A	15	A
Example 5	A	15	A
Example 6	A	15	A
Comparative Example 2	C	25	B

A: Good

B: Slightly poor

C: Poor

[0045] As is apparent from the results shown in Table 3, the printing plates obtained in Examples 4 to 6 are plates which are excellent in sharpness of images, degree of ink buildup (number of inked prints) and storage stability.

[0046]

[Effect of the Invention] The lithographic printing plate

comprising an aluminum support obtained by the present invention is excellent in sharpness of images and ink buildup and is free from sponge residue or contamination of erasure trace, and is also excellent in storage stability.

[Brief Description of the Drawings]

[Fig. 1] Fig. 1 is an electron microscope photograph of the surface of an aluminum plate obtained in Example 1.

[Fig. 2] Fig. 2 is an electron microscope photograph of the surface of an aluminum plate obtained in Example 3.

[Fig. 3] Fig. 3 is an electron microscope photograph of the surface of an aluminum plate obtained in Comparative Example 1.

[Fig. 4] Fig. 4 is an electron microscope photograph of a halftone dot obtained in Example 1.

[Fig. 5] Fig. 5 is an electron microscope photograph of a halftone dot obtained in Comparative Example 1.

[Fig. 1] Photograph substituted for drawing

[Fig. 2] Photograph substituted for drawing

[Fig. 4] Photograph substituted for drawing

Photograph

[Fig. 3] Photograph substituted for drawing, Photograph

[Fig. 5] Photograph substituted for drawing, Photograph

[Amendment]

[Submission Date] October 19, 1993

[Amendment 1]

[Name of Document of Object for Amendment] Specification

[Name of Item of Object for Amendment] Claim 2

[Method of Amendment] Alteration

[Contents of Amendment]

[Claim 2] A method for producing the aluminum support for a lithographic printing plate of claim 1, which comprises performing electrolytic polishing in an electrolytic solution containing hydrochloric acid, boric acid and aluminum ions.

[Amendment 2]

[Name of Document of Object for Amendment] Specification

[Name of Item of Object for Amendment] 0006

[Method of Amendment] Alteration

[Contents of Amendment]

[0006]

[Means for Solving the Problems] The present invention provides an aluminum support for a lithographic printing plate, which is produced by electrolytically polishing an aluminum plate and etching the aluminum plate with an alkali to form pits on the surface, wherein (a) a centerline average roughness Ra of the surface is from 0.05 to 0.25 μm, (b) at least 80% of the surface area is provided with pits having a diameter of 0.01 to 1.5 μm, and (c) surface reflectivity is at least 50%, and a method for producing an aluminum support for a lithographic printing plate, which comprises performing

electrolytic polishing in an electrolytic solution containing hydrochloric acid, boric acid and aluminum ions.

[Amendment]

[Submission Date] December 7, 1993

[Amendment 1]

[Name of Document of Object for Amendment] Specification

[Name of Item of Object for Amendment] 0041

[Method of Amendment] Alteration

[Contents of Amendment]

[0041]

Copolymer of 2-hydroxy-3-phenoxypropyl methacrylate/methyl methacrylate/acrylonitrile/mono(2-methacryloxyethyl)hexahydrophthalate in a weight ratio of 40/30/10/20	3.0 g
2-methoxy-4-hydroxy-5-benzoylbenzenesulfonate of condensate of 4-diazodiphenylamine and formaldehyde	0.3 g
Victoria Pure Blue BOH (manufactured by HODOGAYA CHEMICAL Co., Ltd.)	0.1 g
Malic acid	0.03 g
Ethylene glycol monomethyl ether	90 g
N-N'-dimethylformamide	10 g